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# Parametric Optimization Study of a Lithium-ion Cell

Pramila Rao Nileshwar* , A. McGordon, T.R. Ashwin, and D. Greenwood

*WMG, University of Warwick, Coventry, CV4 7AL, UK*

**Abstract**

Lithium-ion cell technology is well known for its high power and energy density in the automotive application. This paper presents development of a 1D electrochemical model which can be used to predict 18650 lithium-ion cell performance under different operating conditions. COMSOL Multiphysics 5.2a software has been utilized to develop the electrochemical model to predict the cell behaviour under various discharge rates. This tool uses the finite element method (FEM) to solve the conservation equations of charge and species in solid and electrolyte phase. And Butler-Volmer equation for reaction rates of lithium insertion and extraction. In an event that the electrochemical parameters of the cell are not known, determination of these parameters by measurements or experiments is a difficult and challenging task. An attempt has been made in this paper to estimate unknown cell parameters by two methods, first by performing a parametric study on cell parameters such as particle radius, diffusion coefficient, porosity etc. within a known range from literature studies and analyse the sensitivity of these parameters on the model results. Secondly, to improve the accuracy of the simulation results, COMSOL optimization module is used and the simulation results are validated against the experimental data. Apart from the discharge profiles, the proposed model can also be used to study the time dependent distribution of lithium-ion concentration, electrolyte concentration, lithium diffusivity and ionic conductivity in the cell.


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*Keywords:* Lithium-ion cell; Electrochemical model; Parameter optimization

* Corresponding author. Tel.: +44-7721-867311; Fax: +44 (0)24 7652 2943.
*E-mail address:* p.nileshwar@warwick.ac.uk


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## 1. Introduction

For over two decades now, lithium-ion batteries have been studied for application in the automotive sector for energy storage [1]. There has been a growing interest in developing mathematical models of this battery technology to understand the physical processes such as charge transfer reaction, electronic conduction, ionic conduction, solid and solution phase diffusion and the side reactions occurring inside the cell [2].

An electrochemical cell model can assist in determining the electrical limitations and thermal behavior of the cell within a stipulated duration, reducing the time and resources spent on testing to gather the same information. The P2D (Pseudo two dimensional) model, a frequently used electrochemical model, is based on porous electrode theory, concentrated solution theory and kinetics equations and was first developed by Doyle *et al*. [3]. This model has been extended to include energy balance to predict the cell's temperature by researchers Pals *et al.* [4] and later by Gu *et al.* [5].

A crucial part of electrochemical model is the model parameterization. A sophisticated model requires knowing accurately the values of physical properties such as the porosity, electronic conductivity, and lithium diffusion coefficients of each electrode amongst others [6]. Santhanagopalan *et al.* [7] have solved single particle and porous electrode models using Levenberg-Marquardt method to estimate model parameters from four experimental charge/discharge curves at 35℃. An F-test was performed to discriminate between the goodness of fit obtained from the two models and it was found that particle model adequately represented data up to a charge and discharge rate of 1C. The porous electrode model was statistically better than the single-particle model for the 2C rate.

In another work by Jorge *et al*. [8] a methodology based on rigorous model fitting and sensitivity analysis using MATLAB toolbox is presented to determine the parameters of a commercial li-ion pouch cell which showed good agreement with experimental results. Edouard *et al.* [9] have developed a simplified electrochemical-thermal model with sensitivity analysis of all the 41 physical parameters of the cell to predict physicochemical and aging behavior of Li-ion batteries at varying temperature and discharge rates. The model accuracy achieved at high discharge rates is better (4-10 mV) than at low discharge rates (32-181 mV). Another notable study on electrochemical parameter estimation is by Ashwin *et al.* [10], where an implicit finite volume-finite difference formulation is used to re-parametrize the P2D model with known cathode open circuit voltage. With a model accuracy of 2.20 mV RMSE (Root Mean Square Error), this work proves that the electro-chemical model can be easily parametrized for any chemistry.

In the present study, a 1D (one dimensional) electrochemical coupled thermal model for a li-ion cell has been developed where the P2D model equations are solved predominantly along x-axis. The model equations are solved using the finite element commercial software COMSOL Multiphysics (Version 5.2a). The unknown cell parameters have been estimated by two approaches, first by performing a parametric study to estimate the values of the cell parameters and analyze the sensitivity of these parameters on the model results. Second, to improve the accuracy of the model results another attempt has been made using an optimization module and the model results are validated against the experimental data.

## 2. Experimental

A commercial 1.5Ah 18650 Li-ion cell with a graphite anode and a nickel-manganese-cobalt oxide (NMC) cathode was used in this study. The electrolyte is assumed to be a polymer electrolyte with lithium hexafluorophosphate salt in a 1:2 v/v mixture of ethylene carbonate/dimethyl carbonate [3]. All experiments were carried out under constant ambient temperature using Bitrode cell cyclers and Espec thermal chambers. The cell surface temperatures were monitored using J type thermocouples.

## 3. 1D cell model

The schematic of 1D Li-ion cell model, as shown in Fig. 1, consists of a negative copper current collector, a porous negative electrode, ionically conductive but electrically insulated separator, a porous positive electrode, and a positive aluminum current collector. During discharge, positive lithium ions from the negative electrode diffuse through the electrolyte solution to the positive electrode where they react and insert into the solid metal oxide particles. The electrons released from the negative electrode follow the opposite path through an external circuit or load to the positive electrode. During the charging process the reverse electrochemical process occurs.

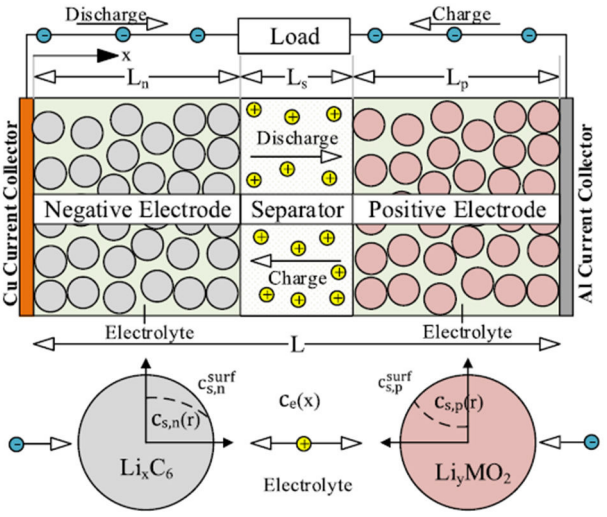



Fig. 1. Schematic of the Li-ion cell model [11]

### *3.1. Governing equations of the electrochemical-thermal model*

The conservation equations used in this 1D electrochemical coupled thermal model of Li-NMC cell are summarized in Table 1 and are referred from Smith *et al.* [12]. Charge transfer kinetics is assumed to follow Butler-Volmer equation.

Table 1. 1D electrochemical model equations [12]

| | Conservation equations | Boundary conditions |
|---|---|---|
| Species, electrolyte phase | $\frac{\partial(\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial x}\left(D_{e_{eff}} \frac{\partial}{\partial x} c_e\right) + \frac{1-t^+}{F} j^{Li}$ | $\frac{\partial c_e}{\partial x}\Big\vert_{x=0} = 0$ , $\frac{\partial c_e}{\partial x}\Big\vert_{x=L} = 0$ |
| Species, solid phase | $\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_s}{\partial r}\right)$ | $\frac{\partial c_s}{\partial x}\Big\vert_{r=0} = 0$ , $-D_s \frac{\partial c_s}{\partial r}\Big\vert_{(r=R_s)} = \frac{j^{Li}}{a_s F}$ |
| Charge, electrolyte phase | $\frac{\partial}{\partial x}\left(k^{eff}\frac{\partial}{\partial x}\emptyset_e\right) + \frac{\partial}{\partial x}\left(k_d^{eff}\frac{\partial}{\partial x} ln(c_e)\right) + j^{Li} = 0$ | $\frac{\partial \emptyset_e}{\partial x}\Big\vert_{x=0} = 0$, $\frac{\partial \emptyset_e}{\partial x}\Big\vert_{x=L} = 0$ |
| Charge, solid phase | $\frac{\partial}{\partial x}\left(\sigma_{eff}\frac{\partial}{\partial x}\emptyset_s\right) = j^{Li}$ | $\sigma_{eff}\frac{\partial \emptyset_s}{\partial x}\Big\vert_{x=0} = \sigma_{eff}\frac{\partial \emptyset_s}{\partial x}\Big\vert_{x=L} = -\frac{I_{app}}{A}$<br>$\frac{\partial \emptyset_s}{\partial x}\Big\vert_{x=L_-} = \frac{\partial \emptyset_s}{\partial x}\Big\vert_{x=L-L_+} = 0$ |
| Energy | $\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + q_r + q_j + q_c$ | $-\lambda \frac{\partial T}{\partial x}\Big\vert_{x=0} = h(T_{amb} - T)$,<br>$-\lambda \frac{\partial T}{\partial x}\Big\vert_{x=L} = h(T - T_{amb})$ |

### *3.2. Numerical procedure*

The electrochemical and thermal model equations are solved simultaneously using a commercial software, COMSOL Multiphysics (Version 5.2a). The software provides pre-built packages of conservation equations and associated boundary conditions and uses the finite element method to solve the constituent partial differential

equations. Five unknowns: $\emptyset_s, \emptyset_e$ (potential in solid and liquid phase respectively), $c_s, c_e$(lithium concentration in the solid and electrolyte phase respectively) and cell temperature, $T$ are solved using time-dependant solver. The finite elements are solved by creating a "mesh" on the geometry.

## 4. Results and Discussion

### *4.1. Validation study*

A 1D model validation study using the well-known cell parameters from Smith *et al.* [12] was carried out in order to determine the accuracy, convergence criteria and the method of solution in COMSOL. Fig. 2 shows the validation study of the base electrochemical model. The 1D simulated results at 1C charge/discharge in an ambient of 25°C are in agreement with results of Smith *et al.* [12] with a model accuracy of less than 10mV RMSE.

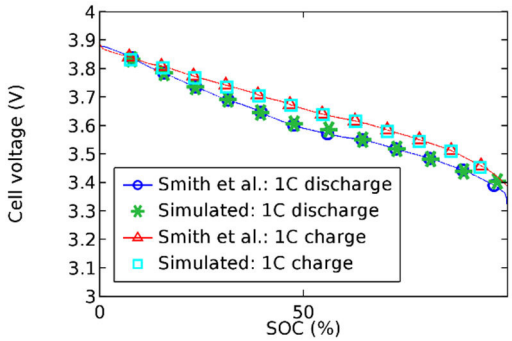



Fig. 2. The base model validation with Smith *et al.* [12] model at 25℃

### *4.2. Optimization study*

The cell was opened to measure the length, width and thickness of electrodes, separator and current collectors using a calibrated micrometer and scale. In the initial study, to determine the unknown cell parameters, a parametric study was conducted by using the measured cell dimensions. The electrochemical cell parameters for Li-NMC chemistry were referred from Fang *et al.* [13]. The sensitivity of the cell parameters were studied using the 'Parametric sweep' study available in COMSOL. Cell parameters such as lithium concentration in electrodes, particle radius, porosity, stoichiometry at 0% and 100% state of charge, and Li-ion diffusivity in electrode were found to have significant effect on the model results.

After identifying the control parameters of the cell, these values were adjusted by using the 'Optimization module' available in the COMSOL software. This module was used to perform parameter estimation, i.e. to adjust model inputs such that the results agree with the experimental data within a defined upper and lower bounds.

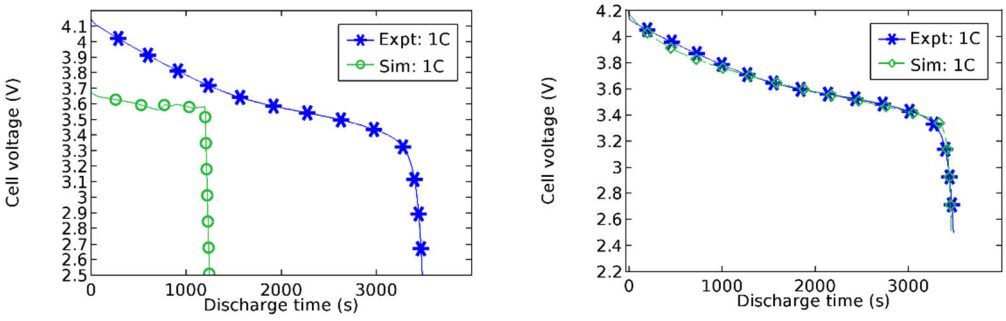
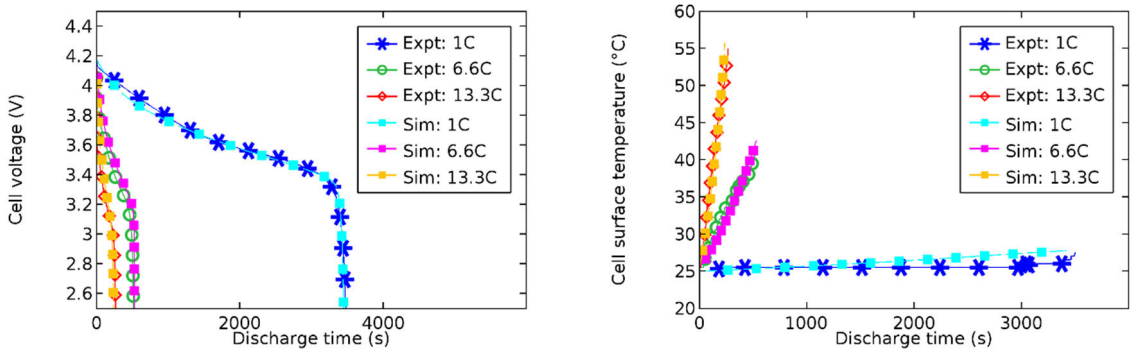



Fig. 3. 1C discharge profile at 25℃ (a) Before optimization (b) After optimization

Fig. 3 (a) displays model result using electrochemical cell parameters from Fang et al. [13] before optimization. The poor quality of cell voltage prediction is clearly evident due to the difference in electrochemical parameters of the cell. Fig. 3 (b) displays model result after optimization for 1C discharge at an ambient of 25℃ where a model accuracy of 13mV RMSE was achieved with optimized cell parameters. The optimized cell parameters are listed in Table 2.

### *4.3. Discharge and Temperature profiles*

Using the optimized cell parameters, the measured and predicted cell voltages are compared as shown in Fig.4 (a) for discharge rates of 1C, 6.6C and 13.3C. The model predictions are in reasonable agreement with the experimental data.




(a) (b)

Fig. 4. (a) Discharge profiles: 1C, 6.6C, 13.3C at 25°C; (b) Temperature profiles: 1C, 6.6C, 13.3C at 25°C

As seen in Fig. 4(b), the predicted cell surface temperature at discharge rates of 1C, 6.6C and 13.3C are also in good agreement with the measured results. As the C rate increases, the joule heat from the contact resistances between current collector and electrodes dominates hence resulting in significant rise of cell temperature. The accuracy of the thermal model is within +1.68℃ RMSE for all the predicted results.

Table 2. 1D electrochemical cell parameters

| Parameter | Negative electrode | Separator | Positive electrode |
|---|---|---|---|
| Thickness, L (cm)* | $90 \times 10^{-4}$ | $20 \times 10^{-4}$ | $60 \times 10^{-4}$ |
| Particle radius, r (cm)** | $1 \times 10^{-4}$ | N/A | $1 \times 10^{-4}$ |
| Porosity (electrolyte phase volume fraction), $\mathcal{E}_e$** | 0.33438 | 0.49924 | 0.33489 |
| Maximum $Li^+$ concentration in solid, $c_{s\,max}$, $mol/cm^3$** | 0.024329 | N/A | 0.031971 |
| Stoichiometry at 0% SOC: $x_{0\%}$ , $y_{0\%}$** | 0.14746 | N/A | 0.93737 |
| Stoichiometry at 100% SOC: $x_{100\%}$ , $y_{100\%}$** | 0.67602 | N/A | 0.31499 |
| Initial electrolyte concentration, $c_e$ ($mol/cm^3$) | $1.2 \times 10^{-3}$ | $1.2 \times 10^{-3}$ | $1.2 \times 10^{-3}$ |
| Reaction rate coefficient, $k_{CT}$ (cm/s)** | $2 \times 10^{-1}$ | N/A | $2 \times 10^{-1}$ |
| Exchange current density, $i_0$ ($A/cm^2$) [3] | $k_{CT}(c_e)^{\alpha a}(c_{s\,max}- c_{s\,e})^{\alpha a}(c_{s\,e})^{\alpha c}$ | N/A | $k_{CT}(c_e)^{\alpha a}(c_{s\,max}- c_{s\,e})^{\alpha a}(c_{s\,e})^{\alpha c}$ |
| Charge-transfer coefficients, $\alpha_a$, $\alpha_c$ [12] | 0.5, 0.5 | | 0.5, 0.5 |
| SEI layer film resistance, $R_{SEI}$ ($\Omega\ cm^2$) | 0 | N/A | 0 |
| Li diffusion coefficient in solid, $D_s$ ($cm^2/s$)** | $2 \times 10^{-10}$ | | $3.9665 \times 10^{-10}$ |
| Electrolyte phase Li diffusion coefficient, | $2.6 \times 10^{-6}$ | $2.6 \times 10^{-6}$ | $2.6 \times 10^{-6}$ |

| | | | |
|---|---|---|---|
| $D_e$ ($cm^2/s$) [12] | | | |
| Bruggeman tortuosity exponent, *p* [12] | 1.5 | 1.5 | 1.5 |
| Solid phase conductivity, σ (S/cm), [12] | 1 | N/A | 0.1 |
| Electrolyte phase ionic conductivity, k (S/cm), [3] | $1.0793 \times 10^{-4} + 6.7461 \times 10^{-3}\ c - 5.2245 \times 10^{-3}\ c^2 + 1.3605 \times 10^{-3}\ c^3 - 1.1724 \times 10^{-4}\ c^4$ | | |
| $Li^+$ transference number, $t^+$ | 0.363 | 0.363 | 0.363 |
| Activation energy for exchange current density, $E^{i0}_{act}$ (J/mol) [13] | 30 000 | N/A | 30 000 |
| Activation energy for solid phase Li diffusion coefficient, $E^{Ds}_{act}$ (J/mol) [13] | 50 000 | N/A | 25 000 |
| Activation energy for electrolyte phase Li diffusion coefficient, $E^{De}_{act}$ (J/mol) [13] | 10 000 | 10 000 | 10 000 |
| Activation energy for ionic conductivity of electrolyte solution, $E^{k}_{act}$ (J/mol) [13] | 20 000 | 20 000 | 20 000 |
| Electrode plate area, A ($cm^2$)* | 843.60 | | |
| Heat transfer coefficient, *h* ($W/cm^2$ K), estimated | 25 | | |
| Reference temperature, (K) | 298.15 | | |

* Measured from cell; ** Obtained from optimization study

## 5. Conclusion

Cell parameters were determined to establish 1D electrochemical Li-ion cell model, first by identifying the sensitive parameters and then applying an optimization method to estimate near accurate values of these parameters. Using the optimized cell parameters an electrochemical coupled thermal model was developed and validated against experimental data for various discharge rates. Good agreement is found between simulation and experimental results for cell voltage and temperature during discharge.

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